[Second Edition.]

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Threads, Ribbons, Tubes and the like from Polyvinyl Compounds.

We, CONSORTIUM FUR ELEKTROCHEMISCHE INDUSTRIE G.M.B.H., a body corporate organised according to the laws of Germany, of 20, Zielstattstrasse, Munich, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In Specifications Nos. 386161 and 393505 we have shown that threads, cords, ribbons, tubes and the like made from polyvinyl alcohol are quite particularly suited for application to medicinal and surgical purposes, and especially for use for stitches and sutures in surgery. An advantage of the polyvinyl alcohol lies in the fact that the parent solutions or the shaped articles therefrom are easily sterilised, so that the threads or the like can be obtained without difficulty in a sterile form and can be used for surgical sutures without causing suppuration or giving rise to the formation of fistulae.

The present invention is the outcome of further development in this field, which has shown that there can be obtained quite generally from polyvinyl compounds which do not contain alcoholic radicals or do not contain exclusively alcoholic radicals, threads, cords, ribbons, tubes and other shaped articles which are useful for medicinal and surgical purposes and especially as substitutes for catgut. Thus for example threads which can be used in substitution for catgut for stitching wounds can be obtained from esters, ethers or acetals of polyvinyl alcohol or from the products of the partial saponification of such esters or acetals, also from esters of polyacrylic acid as polyitaconic acid or from polystyrols.

The possibility of selecting a member of the group of polyvinyl compounds which is especially suitable for the particular medicinal purpose in view considerably extends the applicability of the principle expressed in the aforesaid specifications, namely, by preparing artificial surgical threads or the like from solutions, to attain and ensure freedom from germs and an effective sterility of the products and at the same time to permit suitable modification according to the purpose in view.

As in the case of the polyvinyl alcohols, an internal sterility of the article may be ensured by sterilisation of the solution from which the article is produced and, if necessary, by subjecting the article also to a subsequent sterilisation. Thus the whole process of manufacture, or one more of its specific steps, may be conducted under sterilising conditions, advantageously at temperatures above 100° C.

The possibility of choosing products suited to the purpose is extended by reason of the fact that mixtures or combinations of different polyvinyl compounds with one another or with other substances are also useful for producing surgical threads and the like. For example there come into consideration products of the reaction between polyvinyl acetate and sulphonic acids, such as sulphosalicylic acid.

Although ability to be resorbed is not desired or necessary in all cases, for instance in a substitute for silk for surgical purposes, it is nevertheless of great importance that one should be in a position to impart by suitable additions to polyvinyl compounds which are resorbed not at all or only insufficiently a capacity for being resorbed which can be graded as desired by suitable selection of the magnitude of the addition. The capacity for being resorbed of polyvinyl compounds which are resorbed with difficulty can be increased by the incorporation of water-soluble substances capable of being resorbed, such as gelatine or gums, or substances such as proteins, starch and the like which are regraded by ferments into water-soluble substances. Additions of electrolytes are especially suitable for increasing the capacity for being resorbed. Among the large number of additions which come into question some will now be mentioned. For example organic acids such as oxalic acid, malic acid or lactic acid are active and especially those acids which are substituted by negative or positive radicals. Thus sulpho-salicylic acid, benzene sulphonic acid, toluene

sulphonic acid, trichlor-acetic acid, glycocoll and asparaginic acid are very active. Phenyl-hydrazine hydrochloride is also very active. Inorganic electrolytes such as borax, nickel nitrate, potassium bichromate and others also improve the capacity for being resorbed.

In order to promote the resorbtion of, for instance, polyvinyl acetate there may be added to it sulpho-salicylic acid or benzine sulphonic acid. Resorbtion of polyacrylic acid esters can be promoted by addition of sulpho-salicylic acid. In general an addition amounting to a few per cents, for example 5-10 per cent, is sufficient. The capacity for being resorbed can be graded as required by the magnitude of the addition. If the capacity for being resorbed is too great, the quantity of the addition is diminished and *vice versa*. The substances which promote resorbtion, as well as the further additions hereinafter to be referred to, can be added under suitable circumstances to the parent material serving for the production of the polyvinyl compound. For example, if threads of partially esterified or acetalised polyvinyl alcohol are to be made by spinning a solution of an ester or acetal and subsequently saponifying the threads thus obtained, the additional substances may if required be incorporated in the solution which is to be spun.

In case of necessity the strength of the threads and the like from polyvinyl compounds can also be suitably increased. This object may be attained, for example, by the addition of suitable electrolytes, among which there may be named particularly sulphocyano compounds, such as potassium sulphocyanide or ammonium sulphocyanide. An addition of a sugar, such as cane sugar, also produces a very considerable increase in strength. Additions of about 5-10 per cent suffice, but obviously the quantity can be varied according to requirements and to the desired result.

There also comes into consideration the addition of substances having a bactericidal action. Any bactericidal substance which is compatible with the polyvinyl compound is suitable. From the large number of bactericidal substances of various groups there may be mentioned by way of example esters of aromatic acids, such as propyl benzoate, also salts, compounds or sols of metals such as silver, mercury, bismuth, arsenic and others. Sulphur compounds and other substances having a bactericidal action also come into consideration.

For example, threads of polyvinyl acetate acquire strong bactericidal properties when there is incorporated in them propyl benzoate or mercuric chloride. Even small quantities of these additions generally suffice, depending on their bactericidal action.

There may also be incorporated in the threads therapeutically active substances, for example, substances promoting granulation, such as a silver salt or an iodine preparation, substances having a vasomotor action, such as adrenaline, substances having an astringent or styptic action such as a tanning agent or ferric chloride, tinctures, drugs of any kind, alkaloids, antitoxins, sera, radioactive preparations and so on.

The formed articles in accordance with the invention are mainly of importance in the sphere of surgery. However, the possibility of producing them with a desired capacity for being resorbed and with desired therapeutically active additions also renders them useful, in the form of capsules, pills, plugs and the like, for other medicinal purposes.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. A manufacture of threads, cords, ribbons, tubes and other articles, wherein these articles are made from a polyvinyl compound which contains no alcoholic radicals or does not contain exclusively alcoholic radicals, or from a mixture or combination of such compounds with one another or with other substances, for medicinal and especially for surgical purposes, for instance, as substitutes for catgut, silk, twine, horsehair and other surgical materials for sutures.

2. A manufacture as defined in claim 1, wherein the whole process of manufacturing or one or more of its specific steps are carried out under sterilising conditions advantageously at temperatures above 100° C.

3. Threads, cords, ribbons, tubes and other articles made by the manufacture defined in claim 1 or claim 2.

4. Threads, cords, ribbons, tubes and the like as defined in claim 3, containing a substance which promotes resorbtion, substantially as herein described.

5. Threads, cords, ribbons, tubes and the like as defined in claim 4, containing an electrolyte as a substance which promotes resorbtion.

6. Threads, cords, ribbons, tubes and the like as defined in claim 3, 4 or 5, containing a substance which increases their strength, substantially as herein described.

7. Threads, cords, ribbons, tubes and the like as defined in claim 3, 4, 5 or 6 containing a substance having a bactericidal or therapeutic action.

8. Plugs, pills, capsules and the like made by the manufacture defined in claim 1 or claim 2 and containing or enclosing a therapeutically active substance.

9. Plugs, pills, capsules and the like as defined in Claim 8 and containing also a substance referred to in any of Claims 4-7.

Dated this 16th day of October, 1933.

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